CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Properties of Zinc Oxide

ZnO is a II-VI compound semiconductor of which the ionicity resides at the borderline between covalent and ionic semiconductor. ZnO appears in three types of crystal structure, i.e. wurtzite, zinc blende, and rocksalt, as schematically shown in Figure 2.1. In ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende structure can be formed only by the growth of ZnO on cubic substrate. The rocksalt structure may be obtained at relatively high pressure.

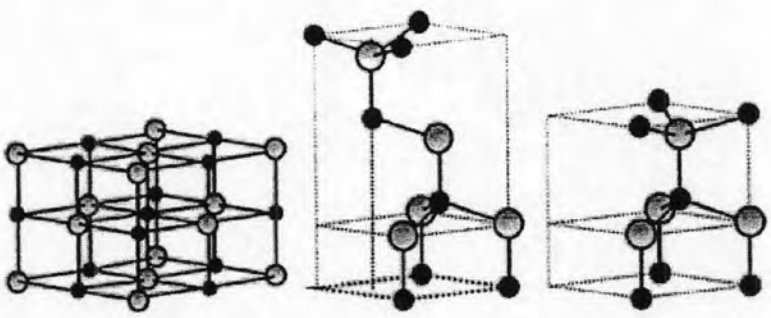

Figure 2.1 Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite. The shaded gray and black spheres denote Zn and O atoms, respectively.

ZnO is an n-type semiconductor with a band gap of 3.37 eV and the free exciton energy of 60 meV, which gives it very high potential for room temperature light emission. This property also gives ZnO strong resistance to high temperature electronic degradation during operation. Therefore, it is attractive for many optoelectronic applications in the range of blue and violet light as well as UV devices

for wide range of technological applications. ZnO also exhibits dual semiconducting and piezoelectric properties. The other properties of ZnO are given in Table 2.1.

Table 2.1 Properties of wurtzite ZnO

Property	*Value*
Lattice parameters at 300 K	
a	0.32495 nm
c	0.52069 nm
a/c	1.602 (ideal hexagonal structure is 1.633)
Density	5.606 g/cm^3
Melting point	1975 °C
Thermal conductivity	130 W/m.K
Linear expansion coefficient (/°C)	*a*: 6.5 x 10^{-6}
	c: 3.0 x 10^{-6}
Static dielectric constant	8.656

Zinc oxide occurs in nature as mineral. Zinc oxide has been prepared in industrial scale by vaporizing zinc metal and oxidizing the generated zinc vapor with preheated air. Zinc oxide has numerous industrial applications. It is a common white pigment in paints. It is used to make enamel, white printing ink, white glue, opaque glasses, and floor tiles. It is also used in cosmetics, pharmaceutical applications such as antiseptic and astringent, dental cements, batteries, electrical equipments, and piezoelectric devices. Other applications are the use as flame retardant, and UV absorber in plastics. Nevertheless, the current major application of zinc oxide is in the preparation of most zinc salts.

2.2 Electrospinning Process

Electrospinning is a process that creates nanofibers through an electrically charged jet of polymer solution or polymer melt. This process is a simple and quick technique for producing fibers of wide range materials with nanoscaled diameters. The process was patented by Formhals in 1934, where the experimental set up was outlined for the production of polymer filaments using electrostatic force. The small diameter provides large surface area to mass ratio, in the range from 10 m^2/g (when the diameter is around 500 nm) to 1000 m^2/g (when the fiber diameter is around 50 nm). Following this investigations of the process have been carried out by a number of researchers. The electrospinning process, in its simplest form, employs a set of equipments consisting of a pipette to hold the polymer solution, two electrodes and a DC voltage supply in the kV range, as shown in Figure 2.2. As strong electric field, as high as several kv/cm, is applied, the polymer droplet from the tip of the pipette is drawn into a structure called a Taylor cone (Li and Xia 2004). Electrostatic charges built up on the surface of a droplet induces to form of a jet, which is subsequently stretched to form a continuous ultrathin fiber (Watthanaarun et al., 2005). The jet is electrically charged and the charge caused the fibers to bend such that every time the polymer fiber loops, its diameter is reduced. In the continuous operation, the number of fibers can be formed within short period of time, as short as a few seconds. The fiber is collected as a web of fibers on the grounded target.

If viscosity and surface tension of the solution are appropriately tuned, varicose breakup is avoided (if there is varicose breakup, electrospray occurs) and a stable jet is formed. A bending instability results in a whipping process which stretches and elongates the fiber until it has a diameter of micrometers or nanometers. The fiber is then deposited on a grounded collector to form non-woven mat that has high surface area (Li and Xia 2004). There are various techniques for collecting oriented fibers, including patterning a collector electrode to cause the fibers to jump between specific positions on the substrate and rotating the substrate to allow deposition of fibers in a spiral or linear pattern.

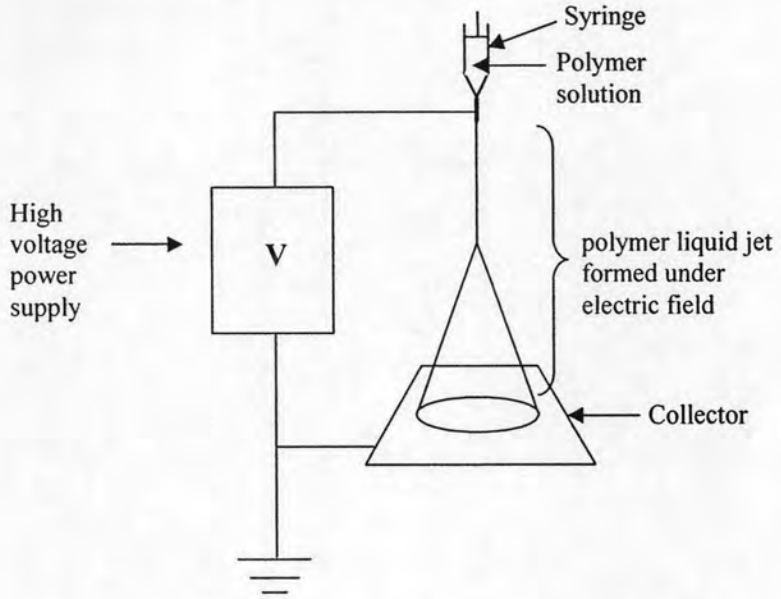

Figure 2.2 Schematic diagram of the electrospinning process.

Important limits of electrospinning are (Ramakrishna et al., 2005):

- Suitable solvent should be available for dissolving the polymer.
- Vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.
- Viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.
- The power supply should be adequate to overcome viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.
- The gap between the pipette tip and the grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form.

2.2.1 Mechanism of Electrospinning Process

The electrospinning process involves polymer science, applied physics, fluid mechanics, electrical engineering, mechanical engineering, chemical engineering, material engineering and rheology. Many parameters, including electric field, solution viscosity, resistivity, surface tension, charge carried by the jet and relaxation time can affect the process. A comprehensive mathematical model of this process was developed by Reneker et al (Reneker et al., 2000).

The electrospinning process consists of three stages: (1) jet initiation and the extension of the jet along a straight line; (2) the growth of a bending instability and the further elongation of the jet, which allows the jet to become very long and thin while it follows a looping and spiraling path; (3) solidification of the jet into nanofibers.

2.2.1.1 Jet initiation and diameter of a single jet

In a typical experiment, a pendent droplet of polymer solution is supported by surface tension at the tip of the spinneret. When the electrical potential difference between the spinneret and the grounded collector is increased, the motion of ions through the liquid charges the surface of the liquid. If the electrical forces at the surface overcome the forces associated with surface tension, a liquid jet emerges from a conical protrusion that formed on the surface of the pendant droplet. The jet is electrically charged. It carries away ions that are attracted to the surface when the potential is applied. Increasing the potential increases both the charge density on the jet and the flow rate of the jet.

The jet diameter decreases with the distance from the orifice. Higher electric fields and a lower surface tension coefficient favor the formation of a thicker jet. Addition of salt (NaCl) to the solution, with other parameters held constant, reduces the diameter of the jet. Increasing the viscosity of the solution does not always increase the diameter. The largest jet diameter occurs when the solution viscosity is in a medium range. Both higher and lower viscosity favors a thinner jet.

2.2.1.2 Bending instability and elongation of the jet

After initiation, path of the jet is straight for a certain distance. Then, an electrically driven bending instability grows at the bottom end of the straight segment. The bending allows large elongation to occur in small region of space. The electrically driven bending instability occurs in self-similar cycles. Each cycle has three steps and it is smaller in scale than the preceding cycle.

The three steps in each cycle are:

Step 1. A smooth segment that is straight or slightly curved suddenly develops an array of bends.

Step 2. As the segment of the jet in each bend elongates, the linear array of bends becomes a series of spiraling loops with growing diameters.

Step 3. As the perimeter of each loop increases, the cross-sectional diameter of the jet forming the loop gets smaller, and the conditions for Step 1 are established everywhere along the loop.

After the first cycle, the axis of a particular segment might lies in any direction. The continuous elongation of each segment is most strongly influenced by the repulsion between the charges carried by adjacent segment of the jet. The externally applied field, acting on the charged jet, causes the entire jet to drift toward the collector, which is maintained at an attractive potential.

2.2.2 Parameters and Conditions for Electrospinning Processs

Variables that must be controlled in order to get uniform fibers via electrospinning include the spinning voltage, the collection distance, and the solution viscosity and conductivity. Proper choice of processing parameters such as surface tension, viscosity, conductivity and concentration of the solution, molecular weight,

applied field and electrode configuration allow the formation of fibers having diameter down to a few nanometers (Li and Xia 2004).

2.2.2.1 Parameters from Polymer Solution

Properties of the polymer solution have the most significant influence on the electrispinning process as well as morphology of the resultant fiber.

Molecular Weight and Solution Viscosity: One of the factors that affect viscosity of the solution is molecular weight of the polymer. Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer having lower molecular weight. Another way to increase viscosity of the solution is to increase the polymer concentration. One of the conditions necessary for the formation of fibers via the electrospinning is that the solution must consist of polymer of sufficient molecular weight or concentration and solution must be of sufficient viscosity. Viscosity has an important role in the formation of smooth fibers. At low viscosity, it is common to find beads along the fibers deposited on the collection plate.

Surface Tension: The initiation of the electrospinning requires the charged solution to overcome its surface tension. The surface tension has a part to play in the formation of beads, which will occur if the solution is not fully stretched, along the fiber length.

Solution Conductivity: The electrospinning involves stretching of the solution caused by repulsion of the charges at its surface. Thus, if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet. The increased charges carried by the solution will increase the stretching of the solution. As a result, smooth fibers are formed instead of beaded fibers. The increase in the stretching of the solution also tends to yield fibers of smaller diameter.

Dielectric Effect of Solvent: Generally, a solution with a greater dielectric property reduces the beads formation, as well as diameter of the resultant electrospun fiber. The bending instability of the electrospinning jet also increases with higher dielectric constant.

2.2.2.2 Processing Conditions

Other important parameters that affect the electrospinning process are the various external factors exerting on the electrospinning jet. These parameters have certain influence on fiber morphology, although they are less significant than the solution parameters (Ramakrishna et al., 2005).

Voltage: The high voltage will induce the necessary charges on the solution. Together with the external electric field, it will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. In most cases, the higher voltage will lead to the greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These factors have the effect of reducing diameter of the fibers and also encourage faster solvent evaporation to yield drier fibers. But at the higher voltage, it has been found that there is a greater tendency for beads formation. Another factor that may influence the diameter of the fiber is the flight time of the electrospinning jet. A longer flight time will allow more time for the fiber to stretch and elongate before it is deposited on the collection plate. Thus, at a lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrospinning jet which may favor the formation of finer fibers.

Feed rate: The feed rate will determine the amount of solution available for electrospinning. When the feed rate is increased, there is a corresponding increase in the fiber diameter or beads size. This is apparent as there is a greater volume of solution that is drawn away from the needle tip. A lower feed rate is more desirable as the solvent will have more time for evaporation.

Temperature: The temperature of the solution has both the effect of increasing the evaporation rate and reducing viscosity of the polymer solution.

Effect of Collector: There must be electric field between the source and the collector for electrospinning to be initiated. Thus, in most electrospinning setup, the collector plate is made out of conductive material such as aluminum foil which is electrically grounded so that there is a stable potential difference between the source and the collector. The charges on the fibers are dissipated thus allowing more fibers to be attracted to the collector. The fibers are able to pack closely together as a result.

Diameter of Pipette Orifice/Needle: A smaller internal diameter has been found to reduce the clogging as well as the amount of beads on the electrospun fibers. The reduction in the clogging could be due to less exposure of the solution to the atmosphere during electrospinning. Decrease in the internal diameter of the orifice was also found to cause a reduction in the diameter of electrospun fibers. However, if the diameter of the orifice is too small, it may not be possible to extrude a droplet of solution at the tip of the orifice.

Distance between Tip and Collector: Varying the distance between the tip and the collector will have direct influence on both the flight time and the electric field strength. For independent fibers to form, the electrospinning jet must have time for most of the solvent to be evaporated. When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the collector plate. Moreover, the electric field strength will also increase at the same time and this will increase the acceleration of the jet to the collector. As a result, they may not have enough time for the solvent to evaporate when it hits the collector. When the distance is too low, excess solvent may cause the fibers to merge when they contact to form junctions resulting in inter and intra layer bonding.

2.2.2.3 Ambient Parameters

Any interaction between the surrounding and the polymer solution may have effect on the electrospun fiber morphology. Since electrospinning is influenced by

external electric field, any changes in the electrospinning environment will also affect the electrospinning process (Ramakrishna et al., 2005).

Humidity: At high humidity, it is likely that water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere. As a result, this may have an influence on the fiber morphology especially for polymer dissolve in volatile solvents. However, an increase in the humidity during electrospining will cause circular pores to form on the fiber surfaces. Humidity of the environment will also determine the rate of evaporation of the solvent in the solution. At very low humidity, volatile solvent may dry rapidly.

Type of Atmosphere: The composition of the gas in the electrospinnig environment will have an effect on the electrospinning process. Difference gases have different behavior under high electrostatic field.

Pressure: When the pressure is below atmospheric pressure, the polymer solution in the syringe will have a greater tendency to flow out of the needle and causes unstable jet initiation. As the pressure decreases, rapid bubbling of the solution will occur at the needle tip. At very low pressure, electrospinning is not possible due to direct discharge of the electrical charges.

2.2.3 Applications of Electrospinning

Nanofibers made from many new synthetic polymers and biologically derived polymers are being considered for the use in tissue engineering, artificial organ applications, drug delivery, and for wound dressings. Nanofibers of DNA were made by Fang and Reneker (Fang and Reneker 1997). The growth of cells on nanofibers was reported by Ko and Reneker (Ko et al., 1998).

Many kinds of bio-generated and bio-compatible materials are currently interested in many fields of applications. Conventional methods for making fibers require so much material that they are often impractical. Electrospinning provides a

convenient way to fabricate nanofibers using as little as a few hundred milligrams of the starting materials.

Nanofibers have found use in filters to remove particles and droplets smaller than 100 nm from liquids or gases. They are also being considered for the absorption of noxious molecules, since their specific surface area is so large, and their surface chemistry can be tailored to be selective to many kinds of substances. The application of pesticides to plants is another area where nanofibers may find large-scale applications. Nanofibers, spun in the field, and directed onto plants by a combination of electrical forces and air stream, will attach to plants with nearly 100% efficiency. This contrasts with the 3 to 5% sticking efficiency of conventional application methods for applying pesticides in form of dusts or sprays. The use of nanofibers to carry and attach pesticides could make the use of sophisticated but expensive pesticides cost effective. The burden placed on the environment by wasted pesticides would also be reduced.

Nanofibers, perhaps at the scale of single polymer molecules, can be expected to play a role in micro-electro-mechanical devices (MEMS). The possibility of making ceramic material by chemical routes that use linear polymers as intermediates provides suggestions for the way to make ceramic nanofibers.

Electrospinning is a simple and versatile method for generating ultrathin fibers from a rich variety of materials that include polymers, composites and ceramic (Dzenis, 2004). Larsen et al. (2003) combined electrospinning with sol-gel method to design vesicles and nanofibers made from inorganic oxide and hybrid (organic/inorganic) materials with diameter in the micrometer and submicrometer range. ZnO nanofibers have also been produced via the electrospinning method, using zinc acetate and poly vinyl alcohol (PVA) as precursors. It has been observed that concentration of zinc acetate and concentration of PVA in the spinning solution affect diameter of the as–spun composite fibers. Examples of report for diameter of composite fibers are given in Table 2.2.

Table 2.2 The literature review of effect of concentration of zinc acetate in PVA solution on PVA/zinc acetate composite fibers

Author	*Concentration of zinc acetate in solution (%wt)*	*Concentration of PVA in solution (%wt)*	*Diameter of composite fibers (nm)*
Yang et al.	5.8	8.5	500
Viswanathamurthi et al.	8.0	9.2	400
Siddheswaran et al.	13.9	10	400 – 500
Wu et al.	25	Not reported	400
	50	Not reported	550
	57	Not reported	600

Yang et al. (2003) prepared ZnO nanofibers by using electrospun PVA/zinc acetate composite fiber as precursor. A voltage of 15 kV was applied to the solution and a dense web of fibers was collected on the aluminium foil. It was confirmed from XRD analysis that the product after calcination at 700 °C was pure ZnO nanofibers with diameters of 50 -100 nm. According to TGA-DTA analysis, all organic species were removed at 550 °C.

Viswanathamurthi et al. (2003) prepared ZnO nanofibers from PVA and zinc acetate by electrospinning technique. A voltage of 19 kV was applied to the solution. The solution was placed in a hypodermic syringe at a fixed distance (15-17 cm) and angle (30°). The fibers were then calcined at 600 °C or 800 °C. Product obtained was pure ZnO nanofibers with diameters of 300 -500 nm. It was observed that diameter of ZnO fibers decreased with increasing calcination temperature. The photoluminescence spectra under excitation at 325 nm showed an ultraviolet emission at 3.13 eV and a green emission at 2.21 eV. These nanofibers could be used as light emitting device in nanoscale optoelectronic applications.

Wu et al. (2005) and Siddheswaran et al. (2006) prepared ZnO nanofibers by electrospinning using polyvinyl alcohol (PVA) and zinc acetate as well. A voltage of 10 - 20 kV was applied to the solution. The solution was placed in a hypodermic

syringe in the range of 13 – 20 cm. The effect of calcination temperature and calcination time was investigated. Product was found to be pure ZnO nanofibers with diameters in the range of 100 - 650 nm. The decrease in diameter of ZnO fibers with an increase in calcination temperature or increase in calcinations time was also observed. However, it was reported that all organic materials were removed at temperature lower than that reported by Yang et al.

2.3 Methods for Synthesizing Zinc Oxide Powder

Zinc oxide particles have been prepared by several methods. In general, the methods which have been reported for zinc oxide include: thermal decomposition method, sol-gel method and precipitation method.

2.3.1 Thermal Decomposition Method

This method has been called differently, e.g. hydrothermal method, glycothermal method and solvothermal method, when different reaction medium is used. Nevertheless, the methods mentioned have been used to successfully synthesize various types of nanosized metal oxides with large surface area, high crystallinity and high thermal stability (Chen et al., 2003; Payakgul et al., 2005; Yang, 2005).

Solvothermal method has been developed to synthesize metal oxide and binary metal oxide via the decomposition of metal-alkoxide precursor in organic solvent. It is principally similar to the hydrothermal method which employs water as the reaction medium. The use of solvent instead of water produces different form of intermediates, of which the stability is not so strong. Instability of the intermediate gives large driving force for the formation of product. Therefore, the synthesis can be accomplished at a relatively low temperature and pressure in a closed system and can be easily controlled. Moreover, it has been applied to successfully synthesize nanocrystalline zinc oxide with and high crystallinity in one step. According to advantages of the solvothermal reaction mentioned above, this method was selected to prepare zinc oxide in this work.

Kunjara et al. (2006) synthesized ZnO with various aspect ratios using various types of organic solvent (alcohols, glycols, n-alkanes and aromatics) at 250-300°C for 2 hours. All products were ZnO in the hexagonal wurtzite structure. The aspect ratio of ZnO primary particles depended upon the solvent employed, such that the aspect ratio increased when the solvent employed had low dielectric constant. The products synthesized in glycols consisted of polyhedral crystals with the lowest aspect ratio, whereas those synthesized in alcohols had moderate aspect ratio and the products

obtained using n-alkane or aromatic compounds as solvent were ZnO nanorods with extremely high aspect ratio.

Tonto et al. (2006) prepared ZnO nanorods by solvothermal reaction of zinc acetate in various alcohols and aromatic compound (1-butanol, 1-hexanol, 1-octanol, 1-decanol, benzene, toluene and xylene) at 250-300°C for 2 hours. All products were ZnO having the hexagonal wurtzite structure. No impurity or secondary phase was observed. The product from the synthesis in alcohol was ZnO nanorods and the length of the rods increased and diameter of the rods decreased when alcohol with longer molecule was employed. It was found that both average diameter and length of ZnO nanorods increased with an increase in either initial concentration of precursor or reaction temperature. The linear relationship between boiling points of organic solvent and aspect ratios of ZnO particles was reported.

2.3.2 Sol-Gel Method

Sol-gel chemistry is based on inorganic polymerization reaction. When ultrafine colloidal dispersions lose fluid, they can turn into a highly viscous mass. Such mass is called a gel. When chemical methods are used to turn solution of metal compounds into gels, it is called sol-gel process. Highly reactive and pure ceramic powders can be prepared from such gels. Two routes are usually described in the literature depending on whether the precursor is aqueous solution of inorganic salt or an alkoxide in organic solvent. Kamalasanan and coworkers (1996) synthesized zinc oxide thin films by the sol-gel technique using zinc acetate as precursor. The XRD pattern showed that the sample was crystallized in hexagonal wurtzite structure. The product was highly transparent without any crack or void. The films showed interference colors depending on its thickness (Kamalasanan et al., 1996).

2.3.3 Precipitation Method

Precipitation method involves the growth of crystals from a solution of different composition. The reactants may or may not be in the same phase before the precipitation take place. If the reactants are in the same phase, the precipitation is

homogeneous, otherwise, it is heterogeneous. The homogeneous precipitation is often preferred because its behavior is more controllable (Chen et al., 1993).

Basically, all process parameters influence quality of the final product of the precipitation. It is usually desired to get the precipitates with specific properties. These properties may involve physical properties of particle such the nature of the phase formed, chemical composition, purity, particle size, surface area, pore size, pore volumes, and separability from the mother liquor. On the other hand, it may include the demands which are imposed by the requirement of downstream processes, such as drying, palletizing or calcinations. It is therefore necessary to optimize the parameters in order to produce the desired material. A variety of particle sizes and shapes can be produced, depending on the reaction conditions. Moreover, the particles can be agglomerates of much finer primary particles. Rodriguez-Paez and coworkers (2001) synthesized zinc oxide nanoparticles by precipitation method, using zinc acetate dihydrate aqueous solutions and nitric acid as reagents. The XRD pattern showed that sample was zinc oxides in hexagonal wurtzite form with crystal size about 50 nm (Rodriguez-Paez et al., 2001).